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X-RAY STRUCTURE DETERMINATIONS OF SOME COMPOUNDS

OF INTEREST IN ANALYTICAL CHEMISTRY

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Summary

A review of the structures of analytically important chelate complexes and chelating molecules which have been determined by X-ray diffraction methods is given. It is suggested that precise structure determinations be made on both the chelating molecule and the complex so that intelligent appraisal can be made of the effect of structure on the formation of specific analytical reagents. With the aid of other data, such as force constants, some of the energetic factors in the formation of chelate complexes might be evaluated.

In this review and progress report only those organic compounds which form chelate complexes with inorganic ions and the complexes themselves are considered. This eliminates discussion of the structures of such substances as acetic acid, which, while of interest to the analytical chemist, do not form chelate complexes. It is not intended that this review cover all chelate complexes since the recent book by Martell and Calvin (7) discusses these in some detail. Very few complete structure determinations on chelate compounds are reported in the literature and there are only two cases where the structure of the chelating molecule and at least one of its complex salts is precisely known.

From the standpoint of the practical analytical chemist, the fundamental question to be answered is, "Can such studies and related studies give sufficient understanding of the factors which influence the formation and stability of chelate complexes so that, at some future time, an organic compound can be designed, a priori, to fit any given analytical situation?" The determinations of exact structures can give only partial answers to such a question and much related data is needed. It is expected that structure studies can give some information on the following points:-

1. The spatial arrangement and configuration of the organic molecule.
2. The bond distances and angles in the compound and complex.
3. The distances between the reacting groups of the organic molecule.
4. The effective diameter of the inorganic ion in each type of complex it may form.
5. The amount and kind of distortion of the organic molecule when a chelate ring is formed with an inorganic ion. If applicable force constants are available then the energy of distortion may be evaluated.
6. The effect of geometry of the organic molecule and the effective diameter of the inorganic ion and its available orbitals on the type and stability of the complexes.
7. The role of water molecules in hydrated crystals.
8. Stabilization of certain resonance forms in the complex.
9. The importance of hydrogen bonds in the formation of complexes.

At the present time there are insufficient data to give any definite answers to any of these points. However, some signs of progress are apparent.

Dimethylglyoxime has been employed as an analytical precipitating agent for nickel for a long time, but its precise crystal structure has just been reported (9). Dimethylglyoxime crystallizes in the triclinic system and has the properties given in Table I as reported by McCrone (8).

Table I

Dimethylglyoxime

Unit cell dimensions
$$a = 6.10A°$$
$$b = 6.30A°$$
$$c = 4.48A°$$
$$\alpha = 122° 31'$$
$$\beta = 90° 6'$$
$$\gamma = 79° 1'$$
Density = 1.353 g.cm.$^{-3}$
Number of Molecules per Unit Cell = 1
Indices of refraction
$$a = 1.40 \pm 0.01$$
$$\beta = 1.54 \pm 0.01$$
$$\gamma = 1.85 \pm 0.01$$
Sign of Double Refraction +

The morphology of the crystal and the absence of any pyroelectric or piezoelectic effect strongly indicate that the crystal is centrosymmetric. This would require each molecule to be centro-symmetrical and thus to have a trans arrangement around the central carbon-carbon bond.
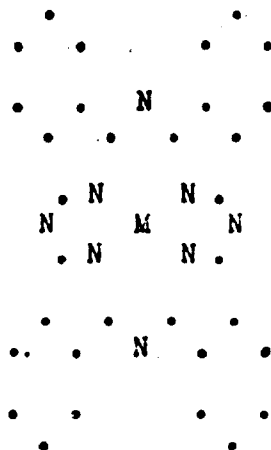
The high index of refraction, γ, is nearly parallel to the axis direction b. This strongly indicates that the C=N bond is directed along b and also the two low indices at right angles indicates a fibrous type of structure. This is further strengthened by observation of a fibrous type of cleavage parallel to b. These guesses are confirmed by the final structure determination, thus pointing out the fact that much information can be derived from optical and very simple X-ray measurements. The final structure of dimethylglyoxime is shown in Figure 1.

In the original paper as presented at the symposium on "X-Rays in Analytical Chemistry" a short discussion of the techniques employed in structure determinations was given. Since that time an excellent review has appeared (17) and such a description of methods will be omitted in this paper.

It is interesting to compare the result for dimethylglyoxime with that for nickel dimethylglyoxime as determined at Iowa State University by Rundle and co-workers (15) and shown in Figure 2. The dimethylglyoxime molecule must first rotate 180° about the central short carbon-carbon bond. This bond has about 25% double-bond character and some energy is therefore required. The central bond is then stretched by 0.09A° and the carbon-nitrogen bond is shortened by about 0.04A°. The nitrogen-oxygen bond remains about the same. Before the final complex is formed the water of hydration of the nickel ion must be removed and a hydrogen ion must be removed from each dimethylglyoxime molecule. A very strong hydrogen bond which Rundle believes to be symmetrical is formed between each pair of oxygen atoms. When proper force constants are known, energies due to these distortions could be calculated. Nickel-nitrogen bonds are very strong and, in nickel phthalocyanine, are even shorter than in this complex. Shorter nickel-nitrogen bonds in the dimethylglyoxime complex or a more nearly square arrangement of the bonds around the central nickel atom would require the oxygen atoms of the two molecules to come even closer together or would require the oxygen and methyl groups to be squeezed toward each other.

Bezzi, Bua and Schiavinato (1,2,3) have given preliminary structural evidence that the cupric dimethylglyoxime complex also exists in the square, coplanar arrangement.

The case of phthalocyanine and its nickel and platinum complexes (10,11,13,14) represents about the only other case where the structures of both the chelating molecule and the complex are completely known. The structures of these compounds can be represented as follows:-

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          •        •
     •    •    .    •    •
     •    •    N    •    •
       •    •    •    •
        . N    N .
      N    M    N
        . N    N .
       •    •    •    •
     •.   •    N    •    •
       •    •    •    •
          •        •
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In the free base (two hydrogen atoms replace the bivalent metal atom) the average carbon-nitrogen distance in the central 16-membered ring is 1.34A°. The distance between one of the four bonding-nitrogen atoms and its two nearest bonding-nitrogen neighbors is 2.65 and 2.76A° in the free base. When the nickel complex is formed, the bonding-nitrogens move in toward the nickel atom by 0.09°A forming nickel-nitrogen bonds of 1.83A°. The average carbon-nitrogen distance in the 16-membered ring increases to 1.38A°. The distance between neighboring bonding-nitrogen atoms becomes 2.56 and 2.60A°. Even in this rather rigid phthalocyanine structure a noticeable amount of distortion has taken place on formation of a nickel complex. In the platinum complex a somewhat different distortion occurs due to the increased size of the platinum ion.

A few other structures of either a complex or a chelating molecule, but not both, have been reported. The structure of zinc 8-quinolinolate dihydrate has been determined in our laboratories at Indiana University. When a zinc ion solution is treated with 8-quinolinol and the solution is neutralized, the dihydrate precipitates. Large crystals can be grown from pyridine-water solutions although most crystals are twinned. Occasionally a single crystal is found. The characteristics of the crystal are shown in Table 2.

Table 2

Zinc 8-quinolinolate Dihydrate

Formula $Zn(C_9H_6ON)_2 \cdot 2H_2O$

Crystal system: monoclinic
  a = 11.28A°
  b = 5.42A°
  c = 13.16A°
  β = 106° 18'
Density = 1.682 (flotation); 1.699 (x-ray)
Number of molecules per unit cell = 2
Space group $P2_1/a$

The two zinc atoms lie at symmetry centers and the molecule must have a trans planar arrangement of the organic part around the central zinc atom. The nearly final result of the structure determination is shown in Figure 3. Because of the heavy atom, the position of the other atoms is less certain and this probably accounts for the irregular interatomic distances in the benzene and pyridine rings. The distances and arrangement around the zinc atom are, however, interesting and are shown schematically in Figure 4. Until the structure of 8-quinolinol itself is determined, little can be said about the distortion involved when the complex is formed.

The hydrated cadmium, lead, cobalt, nickel and copper salts are isomorphous with the zinc salt so that their structures must be very similar to that of zinc 8-quinolinolate dihydrate.

The anhydrous zinc 8-quinolinolate is of the same space group but contains four molecules per unit cell. Thus this molecule may be tetrahedral. This explains the results of Liu and Bailar (6) who were able to resolve the anhydrous zinc salt of 8-quinolinol-5-sulfonic acid. The resolved material racemizes on standing or boiling in water and probably reverts to the planar hydrated structure which does not have optical isomers.

Final least-squares refinements of the structure of the hydrated zinc compound are being made so minor changes may be expected in the bond distances and angles, however the agreement between calculated and observed structure factors is already satisfactory.

At present work on nickel salicylaldoxime is being carried out at Indiana University. The results at the present stage are shown in Figure 5. Here again a planar arrangement of bonds occurs around the central nickel atom. Again, one must await a determination of the structure of salicylaldoxime before making comments on the distortion and geometrical effects upon formation of the complex.

Recently the complete structure determination of two other chelate compounds have been reported. Robertson (12) has reported the structure of cupric tropolone, $Cu(C_7H_5O_2)_2$. The tropolone ring is a regular planar heptagon with an average carbon-carbon distance of 1.40A°, carbon-oxygen distances of 1.25 and 1.34A° and copper-oxygen distances of 1.83 and 1.94A°. The arrangement is square, planar around the central cupric atom.

The structure of cupric acetylacetonate has been reported by Shugam (16). The copper-oxygen bonds are now reported as 1.85 and 1.94A° but probably will become equal on further refinement of the structure. The angle between the oxygen to copper bonds in one molecule is listed as 93°.

Cagle (4) in a preliminary investigation has shown that 2,2'-bipyridine has a trans planar arrangement of the two pyridyl residues in the molecule.

We can make a few tentative observations about the effects of structure of the organic molecules on the formation and stability of complexes at the present time. First, because considerable distortion can occur, the distance between the reacting groups may not be as important as was hitherto supposed. Secondly, rarer types of coordination may occur such as the octahedral coordination around the zinc atom observed in the hydrated 8-quinolinolate complex. This may permit groups to coordinate which otherwise wouldn't be expected to react. Thirdly, a distinction should be made between rather rigid coordinating molecules such as 8-quinolinol where the reacting groups are quite firmly fixed, and other flexible coordinating

molecules such as the amines, dimethylglyoxime, etc. In the case of the rigid molecules the final structure may involve a great distortion of the usual valence bond angles to the metal ion in order to permit the proper bond distances. Fourthly, steric factors are important as are shown by the example of 2-methyl-8-quinolinol. This molecule does not react with the small trivalent aluminum ion as does 8-quinolinol. Irving, Butler and Ring (5) have calculated that the methyl group of one molecule would prevent the close approach of other molecules to the central aluminum atom. Interference should not occur with larger ions.

Acknowledgment

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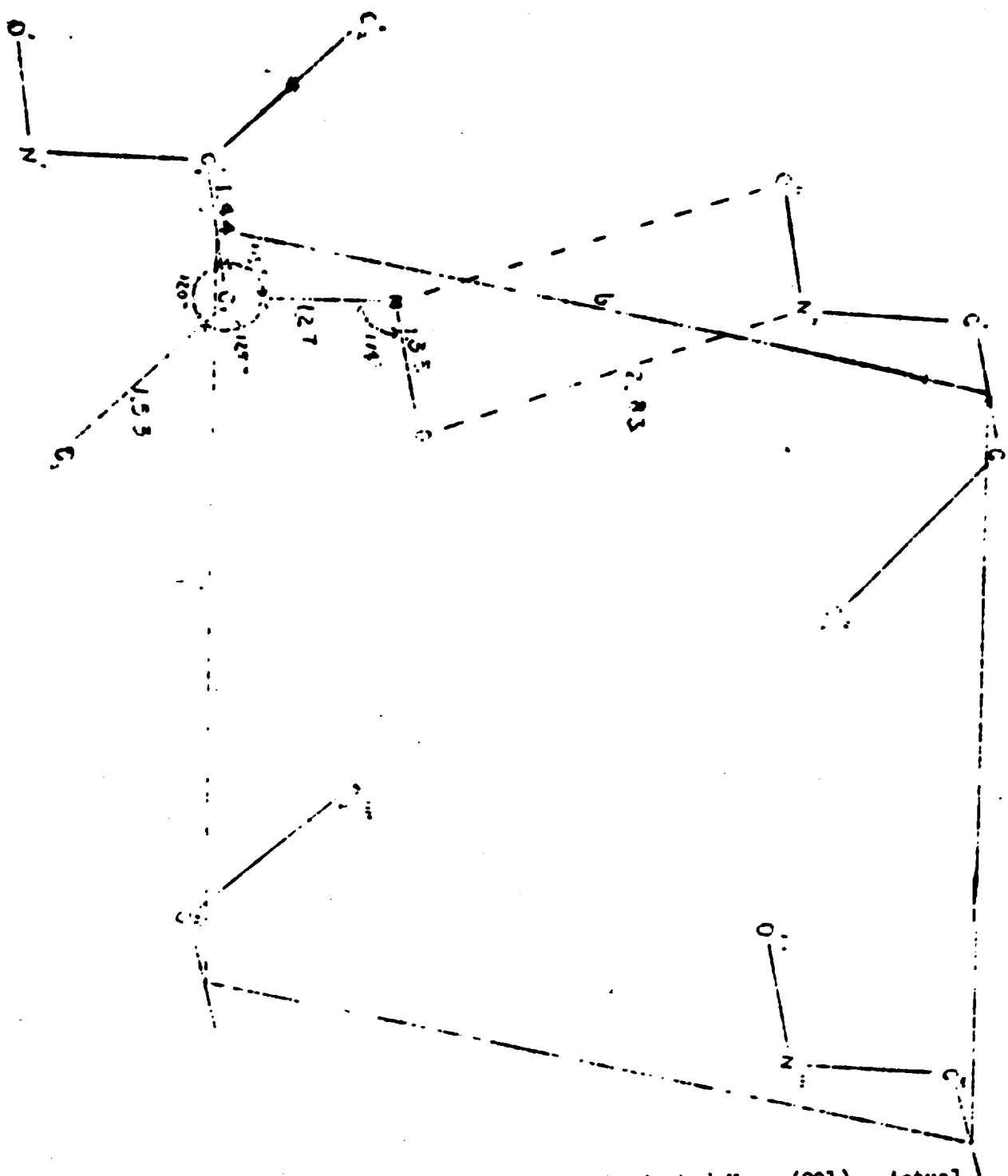17. Staff Report, Chem. and Eng. News, 30, 4356-63 (1952).

Figure 1. Structure of Dimethylglyoxime as Seen Projected Upon (001). Actual Bond Distances (in Angstrom Units) and Angles are Shown.
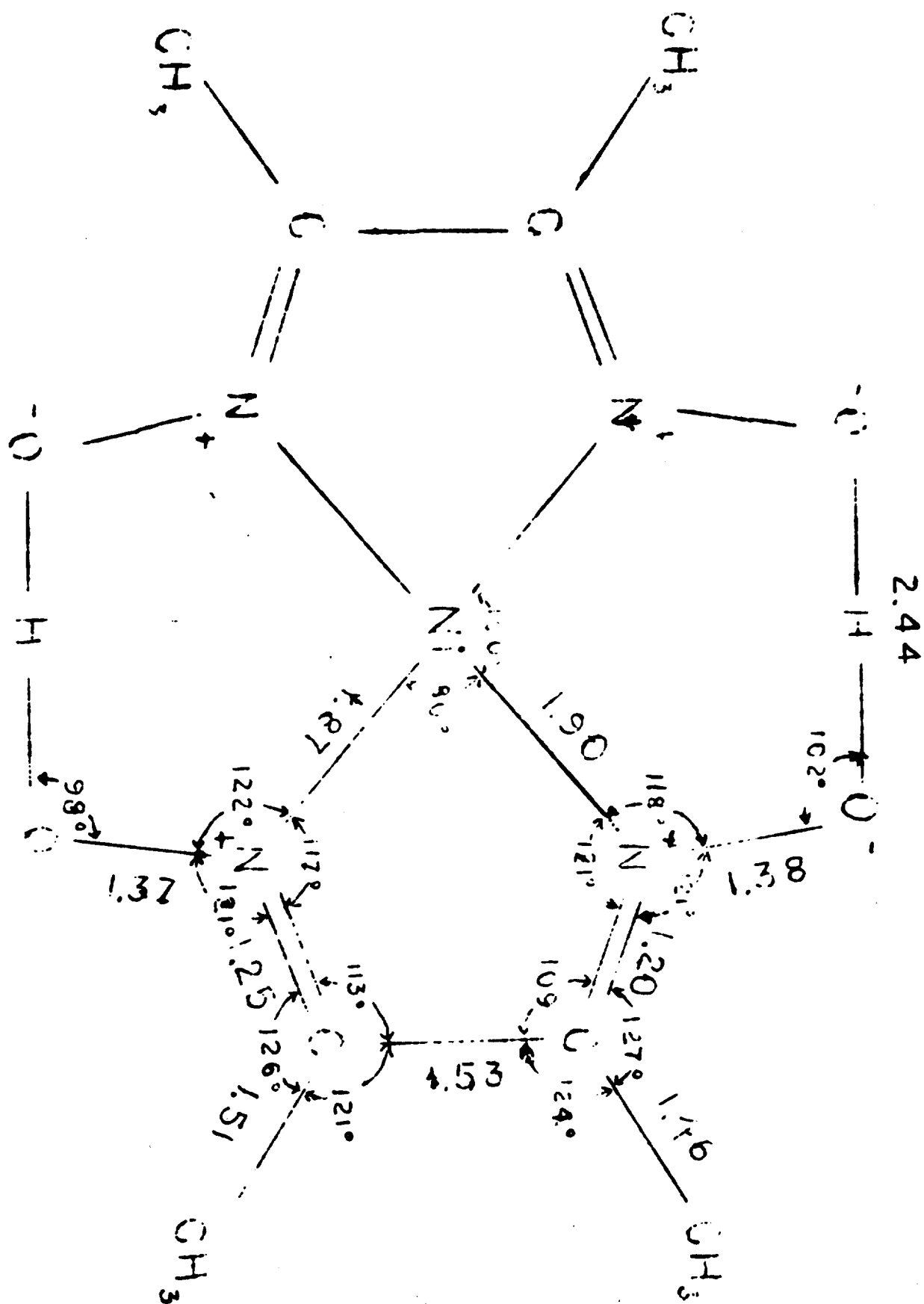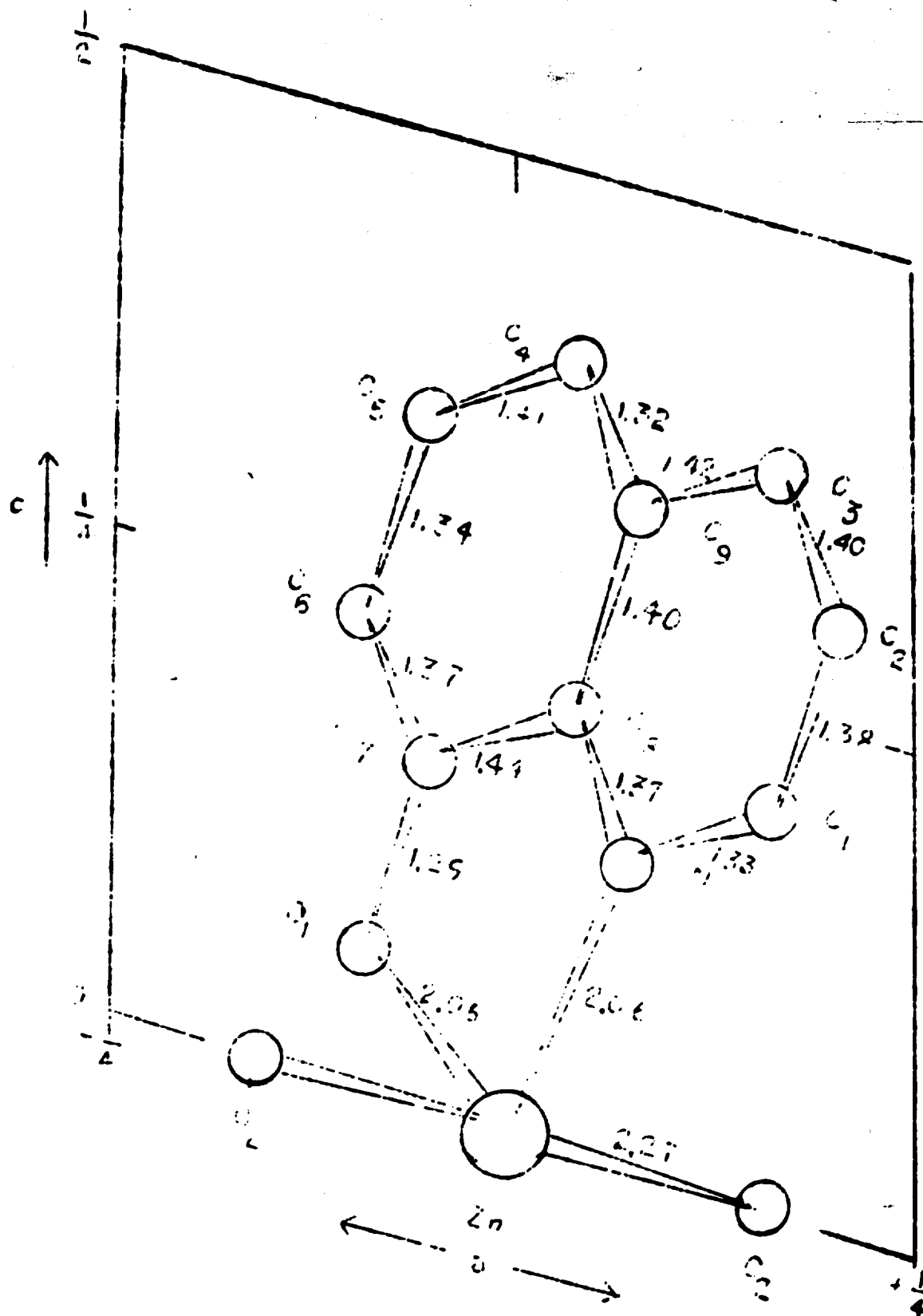
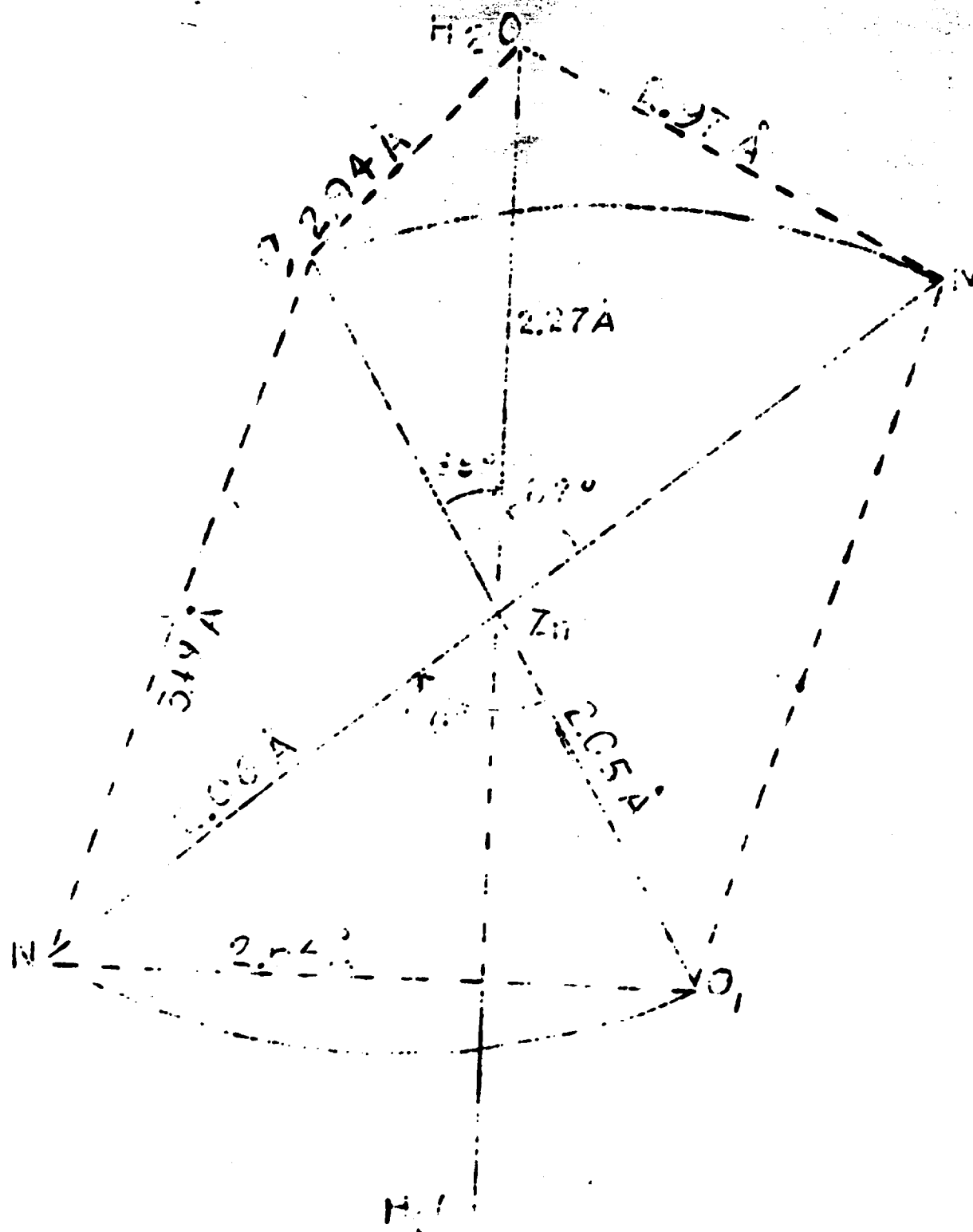Figure 2. Structure of Nickel Dimethylglyoxime. (Courtesy of R. E. Rundle).

Figure 3. Structure of Zinc o-Hydroxyquinolinate Dihydrate as Seen Projected upon (010). Actual Interatomic Distances Indicated in Angstrom Units.

Figure 4. Schematic Representation of Bonds Around Central Zinc Atom in Zinc 8-Hydroxyquinolinate Dihydrate.

Figure 5. Structure of Nickel Salicylaluoxime As Seen Projected Upon (010)
Plane. Distances are Actual Interatomic Distances in Angstrom Units
as Observed at Present Stage of Refinement.